

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

1026



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : C01B 25/12, C01G 28/00, 49/06, C01B 17/74</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 95/11195</b> (43) International Publication Date: 27 April 1995 (27.04.95)</p>
<p>(21) International Application Number: PCT/AU94/00649 (22) International Filing Date: 24 October 1994 (24.10.94) (30) Priority Data: PM 1969 22 October 1993 (22.10.93) AU (71) Applicant (for all designated States except US): CRC FOR WASTE MANAGEMENT AND POLLUTION CONTROL LIMITED [AU/AU]; The University of New South Wales, Botany Street, Gate 11, Kensington, NSW 2033 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): KHOE, Ging, Hauw [AU/AU]; 125 Nicholson Parade, Cronulla, NSW 2230 (AU). EMMETT, Maree, Therese [AU/AU]; 17 Stevens Street, Pennant Hills, NSW 2120 (AU). ROBINS, Robert, G. [AU/AU]; 25 Adelaide Avenue, Lindfield, NSW 2070 (AU). (74) Agent: GRIFFITH HACK &amp; CO.; G.P.O. Box 4164, Sydney, NSW 2001 (AU).</p>		<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).</p> <p>Published With international search report.</p>
<p>(54) Title: PHOTOASSISTED OXIDATION OF SPECIES IN SOLUTION</p> <p>(57) Abstract</p> <p>The invention relates to methods and processes for the photoassisted oxidation of dissolved species such as <u>arsenic</u>, iron, phosphorus and sulphur. Each aspect of the invention involves supplying to a solution including the species to be oxidised, an <u>oxidant</u> and a <u>photoabsorber</u>, and then irradiating the resultant solution with UV/electromagnetic radiation. The resulting oxidised species can then be subsequently treated, used and/or removed (e.g. through precipitation/co-precipitation).</p> <p><i>Photoabsorber = Sulfur Oxidant = Oxygen Species = Arsenic, Iron</i></p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

PHOTOASSISTED OXIDATION OF SPECIES IN SOLUTIONTECHNICAL FIELD

The present invention relates to methods and processes for the photoassisted oxidation of dissolved species including arsenic, iron, phosphorus and sulphur. Particularly, though not exclusively, the invention relates to the treatment of process liquors, waters and waste waters, for example, liquors generated by industries such as the mineral processing and chemical industries and as found in ground waters, in geothermal waters, in leachates from coal fly ash piles, and in acid drainage arising from pyritic heaps resulting from the past practices employed in mining metallic ores, etc.

→ claim 10

claim 17

BACKGROUND ART

Within the above-mentioned industries, there are many impurity bearing aqueous streams. For example streams containing arsenic in the trivalent (+3) oxidation state are found. Known methods of arsenic removal from arsenic-bearing waters include adsorption processes using metal-hydroxide co-precipitation or ion-exchange media, and arsenic precipitation as ferric- or calcium-compounds. When arsenic is in the dissolved state, it is most efficiently removed from aqueous solutions by the above methods when it is present in the pentavalent (arsenate) form. Consequently, there is a need to convert arsenic(III) to arsenic(V) in order to achieve effective arsenic removal from solution.

Furthermore, trivalent (arsenite) compounds have been reported to be fifty times more toxic than the corresponding pentavalent arsenate forms. (In this specification, and in accordance with the IUPAC convention, reference to the terms "arsenic(III)" or "As(III)" will include all arsenite species in which the arsenic is present in the trivalent oxidation state, and reference to the terms "arsenic(V)" or "As(V)" will include all arsenate species in which the arsenic is

Arsenic

- 2 -

present in the pentavalent oxidation state. Similar reasoning applies to the oxidation states for all other species disclosed.)

5 Arsenic(III) compounds in solution can be oxidised to arsenic(V) by dissolved oxygen in ambient conditions only at an extremely slow rate. Hence, stronger oxidants such as chlorine, hydrogen peroxide, and ozone are usually used to convert arsenic(III) to arsenic(V) as part of the arsenic-removal process. In many cases these  
10 oxidants represent the major cost item of the water treatment process.

Furthermore, many of the published methods for the oxidation of arsenic(III) to arsenic(V) have been complex, costly or inappropriate for application on a  
15 large or industrial scale. Many of the reagents used in the oxidation treatment are expensive, as are some of the sources of ionising radiation. Alternatively, the conversion of arsenic(III) to arsenic(V) has not been sufficiently fast enough. Other complexities include the  
20 need for special equipment due to operating parameters such as high pressure, and elevated temperature, the use of electrolysis techniques etc. Clearly, it would be advantageous if a cheaper means was provided for  
oxidising arsenic using a method which can be used at  
25 room temperature and low pressure without the need for special equipment and complex operation.

#### DISCLOSURE OF THE INVENTION

In a first aspect the present invention provides a method for the oxidation of As(III) in solution  
30 comprising the steps of:

- (a) supplying to the solution oxygen, and a photoabsorber which is capable of increasing the rate of As(III) oxidation when exposed to UV radiation; and  
35 (b) irradiating the resulting solution from (a) with UV radiation.

Function of  
photoabsorber



- 3 -

Preferably the photoabsorber is a metal-containing dissolved or solid species, which in one form of the invention can be a dissolved cationic species.

The wavelength(s) of the UV radiation are typically selected such that during irradiation the photoabsorber causes a chemical reaction that increases the rate of oxidation of As(III) by the oxidant relative to a rate where the photoabsorber is absent from the solution. The UV radiation can be sourced eg. from all types of mercury lamps and from sunlight.

Preferably the oxidation is that of As(III) to As(V).

At least preferred forms of the first aspect of the present invention can provide a photoassisted (or photo-enhanced) oxidation process which may enable the more expensive oxidation processes to be replaced by a simple procedure which can be operated at ambient conditions. Thus, expensive chemicals such as hydrogen peroxide, chlorine and ozone may not be required and the process can be used to oxidise, for example, arsenic(III) species in industrial waste waters, process liquors, leachates, dissolved arsenic trioxide from flue dust, and contaminated ground water intended for municipal water supply. The process can also be used for the treatment of geo-thermal/spring waters which often contain arsenic(III) species in solution.

The photoabsorber can be a photo catalyst such as a dissolved species or a solid which absorbs light.

Changes in the oxidation state of the photoabsorber may be acceptable in some applications. Preferably the photoabsorber is iron(II) and/or iron(III) species, but in addition or independently can also be one or more of Al(III), Cr(III), Cu(II), Ce(III) etc as appropriate.

The oxygen can be supplied as pure oxygen or air. Both can be used at pressures greater than 1 atmosphere.

As indicated above, when arsenic(III) is oxidised to arsenic(V), it is considerably easier to remove arsenic

Function of  
photoabsorber →

trace amounts

Definition of  
the photo-  
absorber →

- 4 -

from solution. Preferred methods are precipitation and adsorption processes.

In a second aspect the present invention provides a process for removal of As(III) from solution comprising  
5 the steps of:

- 10 (a) supplying to the solution an oxidant, and a photoabsorber which is capable of both increasing the rate of As(III) oxidation when exposed to electromagnetic radiation and precipitating/co-precipitating with subsequently oxidised As(III);
- (b) irradiating the resulting solution from (a) with electromagnetic radiation; and
- 15 (c) allowing precipitation/co-precipitation of the subsequently oxidised As(III) and the photoabsorber, if necessary, by adjusting the pH of the solution from (b) to cause said precipitation/co-precipitation.

Typically the wavelength(s) of the electromagnetic  
20 radiation are selected such that during irradiation the photoabsorber causes a chemical reaction that increases the rate of oxidation of As(III) by the oxidant relative to a rate where the photoabsorber is absent from the solution.

25 Preferably, in step (c) and if necessary, the pH is adjusted to be greater than about 3.

*Examples of photoabsorbers* → Preferably the photoabsorber is one or more of Fe(II), Fe(III), or Al(III). However, when the photoabsorber is Al(III) it is most preferred that, if  
30 necessary, the pH is adjusted to be greater than about 5.

Preferably, in step (c) and if necessary, the pH is adjusted by adding lime, sodium hydroxide or other base to the solution.

Electromagnetic radiation of wavelengths in the UV  
35 and/or visible light bands is preferably used in the second aspect, although it is most preferred that UV radiation is used. In both the first and second aspects a low, medium or high pressure mercury arc lamp can be

- 5 -

used as the source of UV radiation. As an alternative, UV radiation from a laser source can be used. The process of the second aspect also enables the use of sunlight as a source of electromagnetic radiation.

5 In the second aspect, it is preferred that the oxidant is oxygen, which can be supplied as pure oxygen or air.

} oxidant = O<sub>2</sub>

When irradiating arsenic(III) in the presence of eg. dissolved oxygen and Fe(II)/Fe(III), radiation including specific radiant energy at wavelengths of about 254nm and/or 190nm is preferably used, although for the second aspect other wavelengths extending into the visible region of the solar spectrum may also be used.

10 The electromagnetic radiation can be supplied continuously or in pulses. In some embodiments, a continuous supply should be used because the oxidation reaction stops or slows when the electromagnetic irradiation is stopped whereas a pulse supply is preferably used when the oxidation reaction continues or accelerates for a period after the electromagnetic irradiation is stopped.

When dissolved iron species are used as the photoabsorber, a preferred operating pH for arsenic oxidation in the first and second aspects is a pH of less than 4. At low pH, the iron can be present in solution in its di- and tri-valent states.

25 If the oxidation reaction pH is above 4, then Fe(II) is not stable and is itself oxidised to insoluble ferrihydrite. The oxidation of As(III) still continues, but not as efficiently.

30 Alternatively, other iron hydroxy oxide compounds, magnetic iron oxide or magnetic iron oxide coated with catalytic compound can be used as the photoabsorber at different pH values.

35 Iron(III) is often used as an oxidant in hydrometallurgical processes, eg. the heap leaching of pyritic ores and the acid leaching of uranium ores. Since the rate of oxidation of iron(II) to iron(III) by,

Examples of  
Photoabsorbers →

- 6 -

for example, dissolved oxygen in a low pH (acid) solution is very slow, oxidants such as peroxide, hypochlorite and other oxychloride species have been used. However, these species have attendant handling and environmental  
 5 problems (eg. in disposal, storage etc) and are often costly.

7 In a third aspect the present invention provides a method for oxidising Fe(II) to Fe(III) in a solution having acid pH comprising the steps of:

- 10 (a) supplying to the solution an oxidant, and a substance which is different to Fe(II) and which is both capable of being oxidised and increasing the rate of reaction of Fe(II) to Fe(III) when subject to UV radiation, relative to a rate in  
 15 which the substance is absent from the solution; and  
 17 (b) 18 irradiating the resulting solution from 19 (a) with UV radiation.

20 Most preferably the pH of the solution is about 3.5  
 21 or less.

22 Preferably the substance is As(III), P(III), S(IV),  
 Ce(III) or Mn(II). By using such a substance, the oxidation of Fe(II) to Fe(III) is cheaper than existing  
 25 techniques and generally environmentally more acceptable.  
 26 The wavelengths of UV radiation used can be selected as  
 27 appropriate for the substance supplied.

When the substance is P(III), it is preferred that P(III) is oxidised to P(V) so that the Fe(III) is then  
 30 precipitated as a ferric phosphate.

31 It is most preferred that the oxidant includes  
 32 oxygen, which can be supplied as pure oxygen or air.

As indicated above, the method of the first aspect includes the steps of arsenic(III) oxidation in the presence of oxygen, a photoabsorber and UV radiation.  
 35

Analogously, in a fourth aspect the present invention provides a method for the oxidation of

supplying

Sulfur

Motivation

Claim 13



phosphorus (III) and/or ~~Sulphur~~ <sup>Sulfur</sup> (IV) in solution comprising the steps of:

- 5 (a) supplying to the solution oxygen, and a photoabsorber which is capable of increasing the rate of said oxidation; and
- (b) irradiating the resulting solution from (a) with UV radiation.

10 The method of the fourth aspect has many of the advantages associated with the first aspect of the invention.

The wavelength(s) of the UV radiation are typically selected such that during irradiation the photoabsorber causes a chemical reaction that increases the rate of said oxidation by oxygen relative to a rate in which the photoabsorber is absent from the solution.

20 The photoabsorber can be one or more of iron(II), iron(III), Al(III), Cr(III), Cu(II), Ce(III), etc as appropriate. The UV radiation wavelengths can be selected as for the first aspect. It is also preferred that the oxygen is supplied as either pure oxygen or air.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Notwithstanding any other forms which may fall within the scope of the present invention, preferred  
25 embodiments of the invention will now be described, with reference to the following examples. It should be appreciated, however, that the invention is not limited to the Examples or Figures in which:

Figure 1 depicts the changes in the concentrations  
30 of arsenic(V), iron(II) and dissolved oxygen(DO) as a function of time when a low-pressure mercury lamp (254 nm) was turned on, off and on again while the solution was deoxygenated and re-oxygenated. Initial concentrations: As(III) 50 mg/L, Fe(II) 74 mg/L, pH 1, chloride medium, for the reaction of Example 1;

35 Figure 2 depicts the concentrations of dissolved arsenic(V), iron(II) and oxygen(DO) as a function of

- 8 -

irradiation time. Initial conditions of the aerated solution: As(III) 52.7 mg/L, Fe(III) 74 mg/L, pH 1, chloride medium, for the reaction of Example 2;

Figure 3 depicts the concentrations of dissolved arsenic(V) as a function of time for different solution pHs. Initial conditions of the aerated solution: As(III) 52.7 mg/L, Fe(III) 74 mg/L, chloride medium, for the reactions of Example 3;

\* ← Figure 4 depicts the concentrations of arsenic(V) as a function of time when aerated solutions containing low concentrations of AS(III) were irradiated with UV light (254 nm or 350 nm). Initial concentrations: As(III) 5 mg/L, Fe(II) 74 mg/L, for

- (a) a solution of pH 2 with sulphate as anion; ←
- 15 (b) a solution of pH 1 with chloride as anion;
- (c) a solution of pH 3 with a

(sulphate/chloride anion mixture; ←  
for the reactions of Example 4;

Figure 5 depicts the concentrations of arsenic(V) and iron(II) as a function of solar irradiation time. Initial conditions: As(III) 250 mg/L, Fe(II) 370 mg/L, pH 1, chloride medium, when the solution is exposed to sunlight for the reaction of Example 5;

Figure 6 depicts the concentrations of dissolved arsenic(V) as a function of irradiation time for different photoabsorbers. Initial conditions: As(III) 50 mg/L, mole ratios of the photoabsorber/arsenic(III) 5/1 for Cr(III), 110/1 for Al(III), 4/1 for Cu(II) and 1.6/1 for Ce(III); pH 1, chloride medium, 254 nm UV irradiation, air sparging, for the reactions of Example 6;

Figure 7 depicts the concentration of arsenic(V) as a function of UV irradiation time using a high pressure mercury lamp. Initial conditions: A (Fe/As 2/1, pH 2), B (Fe/As 1/2, pH 2), C (Fe/As 2/1, pH 3), D (Fe/As 4/1, pH 1). Initial As(III) concentration = 250 mg/L in all cases, as set forth in Example 7;

- 8A -

\* { Figure 8 depicts the photoassisted oxidation of 51.5 mg/L of dissolved arsenic(III) in the presence of 72.2 mg/L of iron(II) in sulphate medium (aerated) using 254 nm lamp, followed by the addition of extra iron and lime to remove the arsenic(V) from solution, being an iron co-precipitation process, for the reaction of Example 8; }

Figure 9 depicts the concentrations of iron(II) and phosphorus(V) as a function of time when a solution of 74 mg/L Fe(II) and 20.5 mg/L (P(III)) was aerated and irradiated with 254 nm UV light; chloride medium, pH 1, for the reaction of Examples 9 and 10;

Figure 10 depicts the changes in dissolved iron(II) concentration, in the presence of S(IV), as a function of irradiation time. A 254 nm low-pressure mercury lamp was used to irradiate the air-sparged solution. Initial conditions: Fe(II) 74 mg/L, S(IV) 20 mg/L, pH 1.5; sulphate medium, for the reaction of Examples 9 and 10;

Figure 11 depicts the changes in dissolved iron(II) concentration, in the presence of Mn(II), as a function of irradiation time. A 254 nm low-pressure mercury lamp was used to irradiate the air-sparged solution. Initial concentrations: Fe(II) 74 mg/L, Mn(II) 37 mg/L, pH 1; chloride medium, for the reaction of Example 9; and

Figure 12 depicts the changes in dissolved iron(II) concentration, in the presence of Ce(III), as a function of irradiation time. A 254 nm low-pressure mercury lamp was used to irradiate the air-sparged solution. Initial conditions: Fe(II) 108 mg/L, Ce(III) 50 mg/L, pH 1.5; sulphate medium, for the reaction of Example 9.

MODES FOR CARRYING OUT THE INVENTIONExamples

In the following examples, the following variables were investigated in the evaluation of the photoassisted oxidation of As(III) to As(V), of Fe(II) to Fe(III) of  
5 P(III) to P(V) and of S(IV) to S(VI).

Source of radiant energy.

For As(III), Fe(II), P(III) and S(IV) any artificial source of radiant energy in the UV region of the  
10 electromagnetic spectrum can be used, provided that the radiation is absorbed by the photoabsorber (or  
→ photoactive substance) present. Low and high pressure mercury arc lamps were used. In the second aspect of the invention where visible light can also be used,  
15 blacklight blue, visible fluorescent tubes and sunlight were also investigated.

Low pressure Hg arc lamps emit more than 90% of their radiant energy at a fine 254nm line. Light of this wavelength is strongly absorbed by aqueous ferrous ions  
20 and ferric ions. It was noted that commercial applications for water disinfection and UV oxidation of dissolved organics use similar low pressure lamps because they are the most efficient at converting electrical to radiant energy (up to 50% conversion efficiency).

Source of oxidant.

For the examples below, oxygen is the oxidant during the photoassisted oxidation process. Oxygen was supplied at 0.2 atmosphere partial pressure by aerating the  
30 reaction mixture. Higher partial pressures were achieved by varying the oxygen/nitrogen ratio in the oxygen-nitrogen gas mixture at 1 atmosphere.

It was noted that where the source chosen emitted light at a wavelength at about or below 190nm, ozone was generated from the dissolved oxygen. This did not occur

- 10 -

in the examples below. (Ozone is a powerful oxidant and its reaction with arsenite is well established).

#### Choice of photoabsorber.

It was noted that aqueous arsenite species in solutions did not absorb light above 200nm, hence a photoabsorber was required to absorb the photon's energy. The use of iron and other metal species as a photoabsorber and accelerator for the oxidation reaction was investigated.

Iron was added to the aerated solution as iron(II)- or iron(III)-chloride, sulphate or -perchlorate for experiments with pH<3. Above pH 3, iron(III)-species were present mainly as hydrous iron oxide compounds. The rate of arsenic oxidation was influenced by the initial iron to As(III) ratio. Aluminium(III), Chromium(III), Copper(II), and Cerium(III) may also be used as a photoabsorber.

#### pH.

The reaction mixture pH has a significant effect on the reaction rate and, as indicated above, on the speciation of the photoabsorber. Fe(II) species are stable at pH less than about 3 in the presence of dissolved oxygen.

When the low pressure mercury lamp (254nm) was used for irradiation and dissolved Fe(II) as a photoabsorber, the rate of reaction was increased with a decrease in solution pH.

#### Temperature.

When Fe(II) was used as the photoabsorber, the reaction rate was increased with a decrease in the solution temperature mainly because of the increase in the value of saturation dissolved oxygen concentration with a decrease in solution temperature.

- 11 -

**Light Intensity.**

The reaction rates were dependent on the photon flux when other factors such as dissolved oxygen were not limiting. No reactions of significant rate were observed in the absence of irradiation.

**EXPERIMENTAL EXAMPLES****Photochemical Oxidation of Dissolved Arsenic(III)****EXAMPLE 1**

A reaction mixture (575ml) containing 74mg/L Fe(II) as chloride and 50mg/L As(III) was prepared as follows: the Fe(II) stock solution was obtained by dissolving iron metal powder in HCl solution, the arsenious acid (As(III)) stock solution was obtained by dissolving arsenic trioxide in heated, filtered, demineralised water. The pH of the reaction mixture was adjusted to 1 with the addition of HCl. The reaction mixture was de-oxygenated by bubbling nitrogen and irradiated with light from a 15W Low Pressure Hg lamp (LP Hg lamp). As indicated in Figure 1, where changes in concentrations of As(V) and Fe(II) are shown as a function of irradiation time, no oxidation of As(III) was observed at this stage.

The lamp was then turned off and the solution was re-oxygenated by oxygen-sparging. As indicated in Figure 1, again, no oxidation of iron or arsenic was observed.

After the lamp was switched back on, complete oxidation of As(III) to As(V) was achieved in five minutes. In those five minutes, 80% of the initial Fe(II) was also oxidised to Fe(III). This indicates that both light and oxygen were needed when Fe(II) was used as the photoabsorber.

Actinometry determination using potassium ferrioxalate showed that 2 Watts of 254nm radiation produced by the 15W LP Hg lamp was absorbed by the solution. Total concentrations of Fe, As and other elements were determined using ICP-AES spectroscopy. For low (ppb) concentrations of total As and As(III), atomic

- 12 -

absorption spectroscopy with hydride generation was used. For mg/L levels of As(V), the molybdenum blue spectrophotometric method was used (Johnson D and Pilson M, Anal. Chim. Acta, 58 (1972), 289-299); Fe(II) was determined using a colorimetry method described by Stookey (Anal Chem 42 (1970), 779-781).

#### EXAMPLE 2

A second solution (575ml) containing 74mg/L Fe(III) as chloride (ferric chloride) and 50mg/L As(III) of pH 1 was aerated (with air). When this was irradiated with UV light (254nm), as above, complete oxidation of As(III) was achieved in 30 minutes (Figure 2). No significant reaction of Fe(III) to Fe(II) was observed, indicating that oxygen, not iron, was the oxidant.

#### \* EXAMPLE 3

Four reaction mixtures, each (575ml) containing 74 mg/L Fe(III) as sulphate (ferric sulphate) and 50mg/L As(III), were prepared at several pH values (pH 1, 3, 6 and 11) and aerated with air. When the solution was above pH 5, carbon dioxide-free air was used in order to achieve constant pH readings. The initial dissolved As(III) in all the reaction mixtures was oxidised to As(V) only after they were irradiated with the 15W LP Hg lamp (Figure 3). This indicates that the reaction proceeds in the presence of sulphate (chloride was used in previous examples) and in alkaline as well as in neutral and acid conditions.

#### EXAMPLE 4

Two reaction mixtures were prepared with 5mg/L As(III) and 74mg/L Fe(II). The first mixture was of pH 2 with sulphate as the anion. The concentrations of Fe(II), As(III) and  $H^+$  in this solution would be similar to those found in some acid mine drainage effluents arising from heaps of mining wastes containing arsenopyrite.

Photoabsorber

To be removed

source of Sulphur used to oxidize As(III)

- 13 -

The second mixture was of pH 1 with chloride as the anion. Both mixtures were irradiated using the low pressure mercury arc lamp as above.

On irradiation, complete oxidation of the  
5 arsenic(III) initially present in the reaction mixtures was achieved in less than 10 minutes (Figure 4). This indicates that low concentrations of As(III) can be completely oxidised in short time. In contrast, it is known that the oxidation rate of As(III) using  
10 conventional oxidants, such as hydrogen peroxide, is dependent upon the As(III) concentration. Hence they are slow to oxidise the final fraction of As(III). Because the photochemical method is effective at oxidising low concentrations of arsenic(III), complete oxidation of  
15 larger initial concentrations of As(III) can be achieved in reasonable time.

Furthermore, results from optimisation/screening experiments show that the photoassisted reactions favour the oxidation of arsenic(III) in preference to reductants  
20 which are usually present in acid drainage waters such as ferrous species. These species, together with partially oxidised sulphur species, represent an extra chlorine- or peroxide-demand in conventional oxidation processes.

A third reaction mixture (750ml), containing 74mg/L  
25 Fe(III), a 1/1 sulphate to chloride anion ratio, and of pH 3, was irradiated with light from a 20W blacklight blue (BLB) fluorescent tube. Actinometry determination using ferrioxalate showed that the solution absorbed 2.9W  
of light assuming the band of wavelengths are evenly  
30 distributed around 350nm. Complete oxidation of the arsenic(III) initially present in the reaction mixtures was achieved in 10 minutes.

As blacklight blue tubes emit a near ultraviolet spectrum similar to sunlight, laboratory experiments with  
35 this lamp were performed for the simulation of experiments involving solar irradiation in the field.



- 14 -

Photochemical oxidation of As(III) using sunlight

EXAMPLE 5

5 A litre of reaction mixture containing 370mg/L Fe(II) and 250mg/L As(III) in pH1.5 HCl was aerated and circulated through a white tray of 20 x 20 cm. The experiment was conducted in Sydney, Australia, at noon, on 16 February 1994. Complete oxidation of the arsenite was achieved in 100 minutes (Figure 5).

Photoabsorbers other than iron

10 EXAMPLE 6

Other metals can also be used as photoabsorbers. Figure 6 shows the progress of oxidation of arsenite (50mg/L) where other metals were used as the photoabsorber in place of iron. In the absence of  
15 irradiation, these species will not oxidise arsenite.

The molar metal:As ratio was 1.6, 5, 110 and 4 for Ce(III), Cr(III), Al(III) and Cu(II) respectively. The pH was 1 and chloride was the accompanying anion. The low pressure mercury lamp was used. Metals such as  
20 divalent Mn, Ni and Zn do not absorb ultraviolet light at 254nm.

EXAMPLE 7

A high pressure mercury lamp was used as the source of light for the experiments shown in Figure 7. Four  
25 solutions, each of 200mL, with different Fe(II)/As(III) ratios and pH as shown in the table below (chloride medium) were irradiated. Different rates of oxidation were observed. Run D gave the fastest rate ie. the initial As(III) concentration of 250mg/L was completely  
30 oxidised in less than 30 minutes.

- 15 -

	A	B	C	D
Fe/As ratio	2/1	1/2	2/1	4/1
pH	2	2	3	1

### Interfering Substances

As(III) oxidation rate is reduced if the optical density of the solution is increased by the presence of other species which absorb ultraviolet light eg. dissolved conjugated organic compounds or excessive iron(III) concentrations. Screening tests indicated that the reaction rate is not significantly reduced by the presence of soil organics such as fulvic acid (8mg/L). Sulphur(IV) as sulphite also did not significantly affect the rate. Heavy metals such as nickel chromium zinc manganese and copper were not found to reduce the rate. The reaction is faster if chloride or perchlorate electrolyte is used in place of sulphate. Carbonate introduced by aerating alkaline solutions has no observable effect on the reaction rate. Calcium and magnesium do not interfere with the reaction so wastes previously stored as calcium arsenite may be successfully treated.

### Photochemical Oxidation and Removal of Dissolved Arsenic(III)

#### EXAMPLE 8

A solution (575ml) containing 30mg/L As(III) and 74mg/L Fe(II) as sulphate (pH 2) was aerated (with air) and irradiated with UV light (254nm). The oxidation of As(III) to As(V) was completed in 15 minutes (Figure 8).

After the photoassisted oxidation process was completed, extra iron was added, as Fe(III) sulphate (alternatively, Fe(II)-chloride or used pickle solution from the steel industry can also be used because at pH > 3.5 Fe(II) is oxidised to Fe(III) by dissolved oxygen in aerated solution) to give an Fe-to-As mole ratio of about

- 16 -

7, and lime was added to give a final pH 5 (the optimum pH for arsenic removal using iron co-precipitation). The residual dissolved (total) arsenic concentration was found to be 0.008mg/L (the World Health Organisation guideline for drinking water for arsenic is 0.050mg/L).

→ trace amount

For comparison, when the photooxidation process was not included, using the same iron co-precipitation process, the total residual arsenic concentration was found to be 8.5mg/L ie. a 1000-fold factor greater than when the As(III) was first photochemically oxidised.

The oxidation and removal process can also be applied to the treatment of pyrometallurgical flue dusts (eg. from the roasting of arsenopyritic ores) which can contain more than 50% arsenic trioxide. It was proposed to extract the flue dust using hydrochloric acid (HCl) and to add iron(II) solution before irradiation or, alternatively, using pickle solution from the steel industry which is usually rich in HCl and ferrous ions.

The flue dust extract, which was obtained by leaching the flue dust with 0.1M HCl overnight, contained 600mg/L As(III) and iron was added to give a concentration of 70mg/L Fe(II). Using UV irradiation from the LP Hg lamp above and aerated with air, the oxidation step was completed in less than 60 minutes.

After the addition of extra iron to give a Fe/As mole ratio of 7/1 and neutralisation with lime to pH7, the concentration of dissolved arsenic in the water was reduced from 600mg/L in the flue dust extract to 0.045mg/L. For comparison, when the oxidation step was not included, the residual dissolved arsenic in the treated water was 0.450mg/L. Co-precipitation pH of 7 was used, instead of the optimum for arsenate removal (pH 5), because pH 5 would have been too low for the removal of heavy metals which are usually present in flue dust.

- 17 -

**Photochemical Oxidation of Iron(II) at pH<3****EXAMPLE 9**

It is known that, in the absence of UV irradiation, the oxidation rate of Fe(II) to Fe(III) by oxygen at pH less than about 3 is very slow. As already mentioned above, and shown in Figures 1 and 5, when Fe(II) was used as the photoabsorber for the photoassisted oxidation of As(III), it was also oxidised to Fe(III).

Further experiments showed that other metals and non-metals can be used to increase the rate of oxidation of Fe(II) to Fe(III). As depicted in Figures 9 to 12, the presence of dissolved phosphorus(III) which was added as  $H_3PO_3$ , ~~Sulphur(IV)~~ which was added as sodium sulphite, manganese(II) which was added as manganous chloride, or, cerium(III) which was added as cerium(III)-sulphate increased the rate of oxidation of Fe(II) when irradiated using a low pressure mercury lamp.

**Photochemical Oxidation of P(III) and S(IV)****EXAMPLE 10**

It was observed that during the experiments whose results are shown in Figures 9 and 10, P(III) and S(IV) were oxidised in the same manner as As(III) ie. P(III) to P(V) and S(IV) to S(VI).

The following results were observed:

Photoassisted oxidation of S(IV) to S(VI)

	Before irradiation	After 30 minutes irradiation
S(IV)	20	14.2
S(VI)	0	5.8

- 18 -

## Photoassisted oxidation of P(III) to P(V)

	Before irradiation	After 100 minutes irradiation
P(III)	20.5	11.66
P(V)	0	8.84

**Proposed Use of Methods and Processes**

5      **First and second aspect of the invention: Oxidation and removal of dissolved arsenic(III)**

As discussed above, this aspect of the invention is versatile, in that it can be used to rapidly achieve complete oxidation of arsenic in solutions with either high or low initial arsenic(III) concentrations. Hence, the projected commercial applications of this invention are:

- The dissolution and oxidation of arsenic trioxide contained in metallurgical flue dust as an initial process for arsenic recovery or for the eventual disposal as iron(III)-arsenate compounds. Arsenic trioxide and other forms of arsenic(III) are frequently a waste-product of the mining and extraction of metals such as copper, gold, lead, nickel and zinc.
- The oxidation and removal of dissolved arsenic(III) from:
  - leachates arising from heaps of coal fly ash
  - acid drainage from piles of pyritic material arising from mining operations
  - ground water or geothermal/spring waters.

**Third aspect: Oxidation of iron(II) in acid solution**

Iron(III) in acid solution is commonly used as an oxidant for use in hydrometallurgical processes, for example the oxidative leaching of uranium ores and heap leaching of ores. Currently, oxidants such as peroxide- or chlorine-compounds are used for the re-oxidation of iron(II) in the leaching circuit. The photoassisted

*Trace amounts*

- 19 -

oxidation of iron(II) by dissolved oxygen can be used as an alternative to these oxidants.

**Fourth aspect: Oxidation of phosphorus(III) and sulphur(IV)**

5 Dissolved iron is a common impurity in hydrometallurgical process liquors. If it is present as Fe(II) in acid solution, the addition of P(III), say as phosphorous acid or its salt, and irradiation using UV lamps or sunlight can precipitate out the iron impurity  
10 as ferric phosphate.

15 Sulphur(IV) as sulphurous acid (dissolved SO<sub>2</sub> gas) or its salt can be used as an adjunct (like phosphorous species) in the photoassisted oxidation of Fe(II) in acid solution. Alternatively, this aspect of the invention can be used to treat/process effluents, waters or process liquors by converting the sulphurous species to sulphate. Uncontrolled oxidation of partially oxidised sulphur species in the environment can result in the lowering of  
20 pH with the attendant problems of heavy metal immobilisation.

iron as impurity  
species

Sulfur used

- 20 -

CLAIMS

1. A method for the oxidation of As(III) in solution comprising the steps of:
  - (a) supplying to the solution oxygen, and a photoabsorber which is capable of increasing the rate of As(III) oxidation when exposed to UV radiation; and
  - (b) irradiating the resultant solution from (a) with UV radiation;
2. A method for the oxidation of phosphorus(III) and/or sulphur(IV) in solution comprising the steps of:
  - (a) supplying to the solution oxygen, and a photoabsorber which is capable of increasing the rate of said oxidation when exposed to UV radiation; and
  - (b) irradiating the resulting solution from (a) with UV radiation.
3. A method as claimed in claim 1 or claim 2, wherein the photoabsorber is a metal-containing dissolved or solid species.
4. A method as claimed in claim 3, wherein the photoabsorber is a dissolved cationic species.
5. A method as claimed in any one of the preceding claims, wherein the photoabsorber is selected from one or more of Fe(II), Fe(III), Al(III), Cr(III), Cu(II) and Ce(III).
6. A method as claimed in any one of the preceding claims, wherein the oxygen is supplied to the solution in the form of air or as pure oxygen.

- 21 -

7. A method as claimed in any one of the preceding claims, wherein the oxygen is supplied to the solution at a pressure of or greater than ambient, or at a partial pressure of or greater than 0.2 atmospheres.

5 8. A process for removal of As(III) from solution comprising the steps of:

10 (a) supplying to the solution an oxidant, and a photoabsorber which is capable of both increasing the rate of As(III) oxidation when exposed to electromagnetic radiation and precipitating/co-precipitating with subsequently oxidised As(III);

(b) irradiating the resulting solution from (a) with electromagnetic radiation; and

15 (c) allowing precipitation/co-precipitation of the subsequently oxidised As(III) and the photoabsorber, if necessary, by adjusting the pH of the solution from (b) to cause said precipitation/co-precipitation.

20 9. A process as claimed in claim 8, wherein the oxidant is oxygen and is supplied to the solution in the form of pure oxygen or air.

25 10. A process as claimed in claim 9, wherein the oxygen is supplied to the solution at a pressure of or greater than ambient, or at a partial pressure of or greater than 0.2 atmospheres.

11. A process as claimed in any one of claims 8 to 10, wherein, in step (c) and if necessary, the pH is adjusted to be greater than about 3.

30 12. A process as claimed in any one of claims 8 to 11, wherein the photoabsorber is one or more of Fe(II), Fe(III), or Al(III).



- 22 -

13. A process as claimed in claim 12 wherein, when the photoabsorber is or includes Al(III), the pH in step (c), if necessary, is adjusted to be greater than about 5.
- 5 14. A process as claimed in any one of claims 8 to 13, wherein, in step (c) and if necessary, the pH is increased by adding lime, sodium hydroxide or other base to the solution.
- 10 15. A method or process as claimed in any one of claims 1 to 14, wherein in steps (a) and (b) the pH is less than about 4.
16. A method for oxidising Fe(II) to Fe(III) in a solution having acid pH comprising the steps of:
- 15 (a) supplying to the solution an oxidant, and a substance which is different to Fe(II) and which is both capable of being oxidised and increasing the rate of reaction of Fe(II) to Fe(III) when subject to UV radiation, relative to a rate in which the substance is absent from the solution; and
- 20 (b) irradiating the resulting solution from (a) with UV radiation.
17. A method as claimed in claim 16, wherein the pH of the solution is about 3.5 or less.
- 25 18. A method as claimed in claim 16 or claim 17, wherein the substance is As(III), P(III), S(IV), Ce(III), or Mn(II).
19. A method as claimed in any one of claims 16 to 18, wherein, when the substance is P(III), irradiating of the resulting solution from (a) with UV radiation causes
- 30

- 23 -

P(III) to be oxidised to P(V) such that Fe(III) formed in the method precipitates as ferric phosphate.

20. A method as claimed in any one claims 16 to 19, wherein the oxidant is oxygen, and is supplied in the  
5 form of either pure oxygen or air.

21. A method as claimed in claim 20, wherein the oxygen is supplied to the solution at a pressure of or greater than ambient, or at a partial pressure of or greater than 0.2 atmospheres.

10 22. A method or process as claimed in any one of the preceding claims, wherein the radiation includes specific radiant energy at wavelength(s) of about 254nm and/or 190nm.

15 23. A method or process as claimed in any one of the preceding claims wherein the electromagnetic radiation is, or the UV radiation is from, sunlight.

FIGURE 1

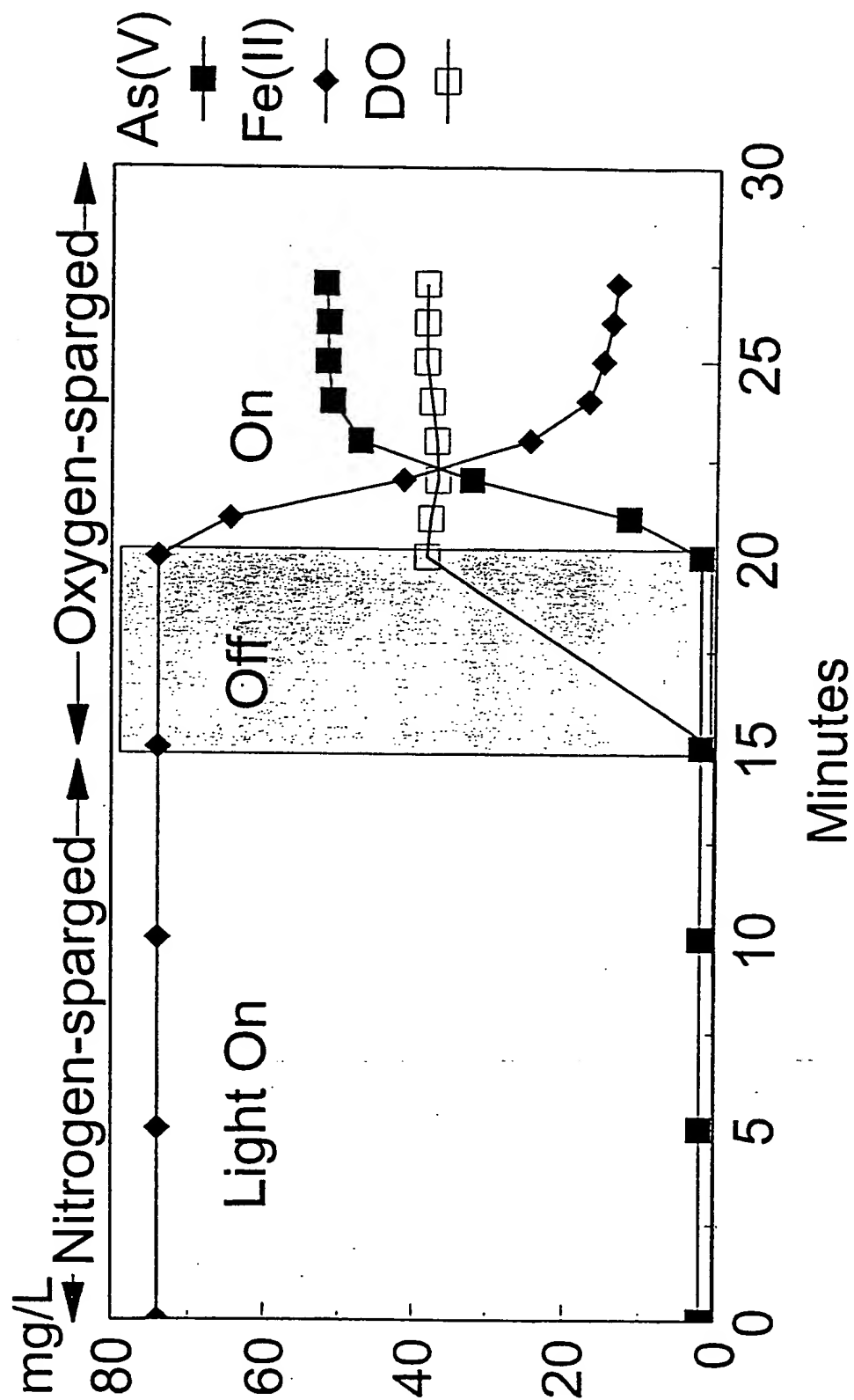


FIGURE 2

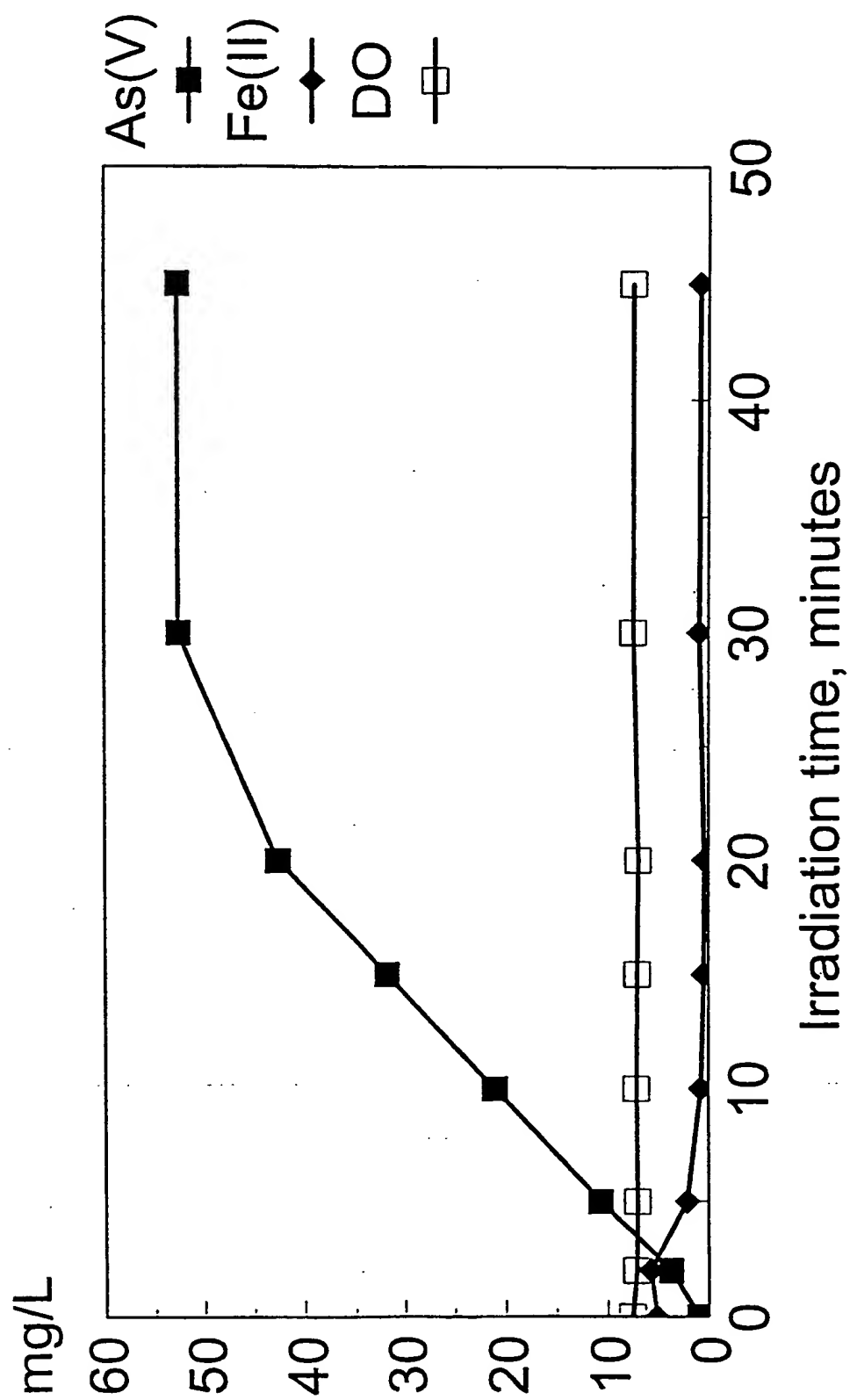


FIGURE 3

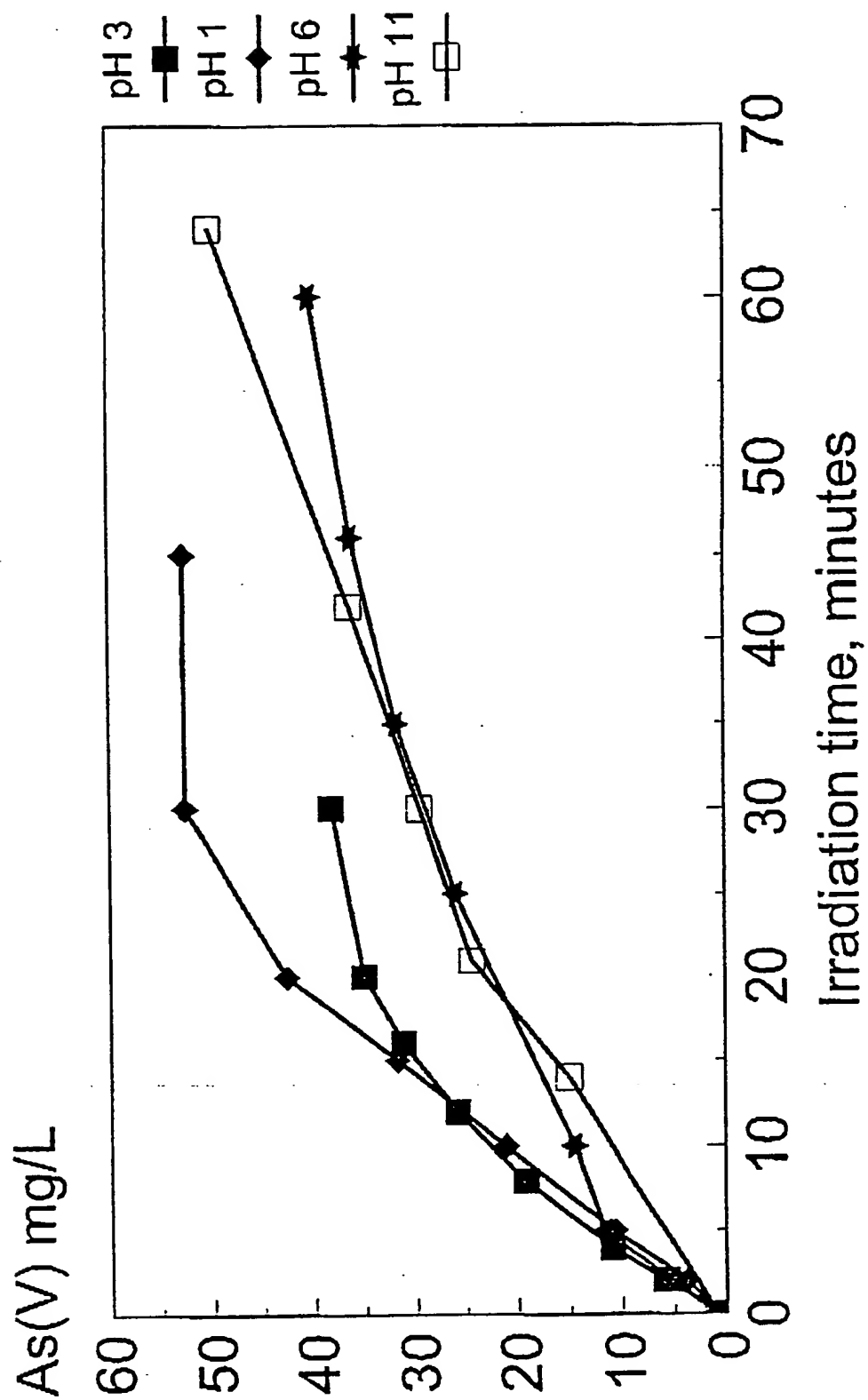
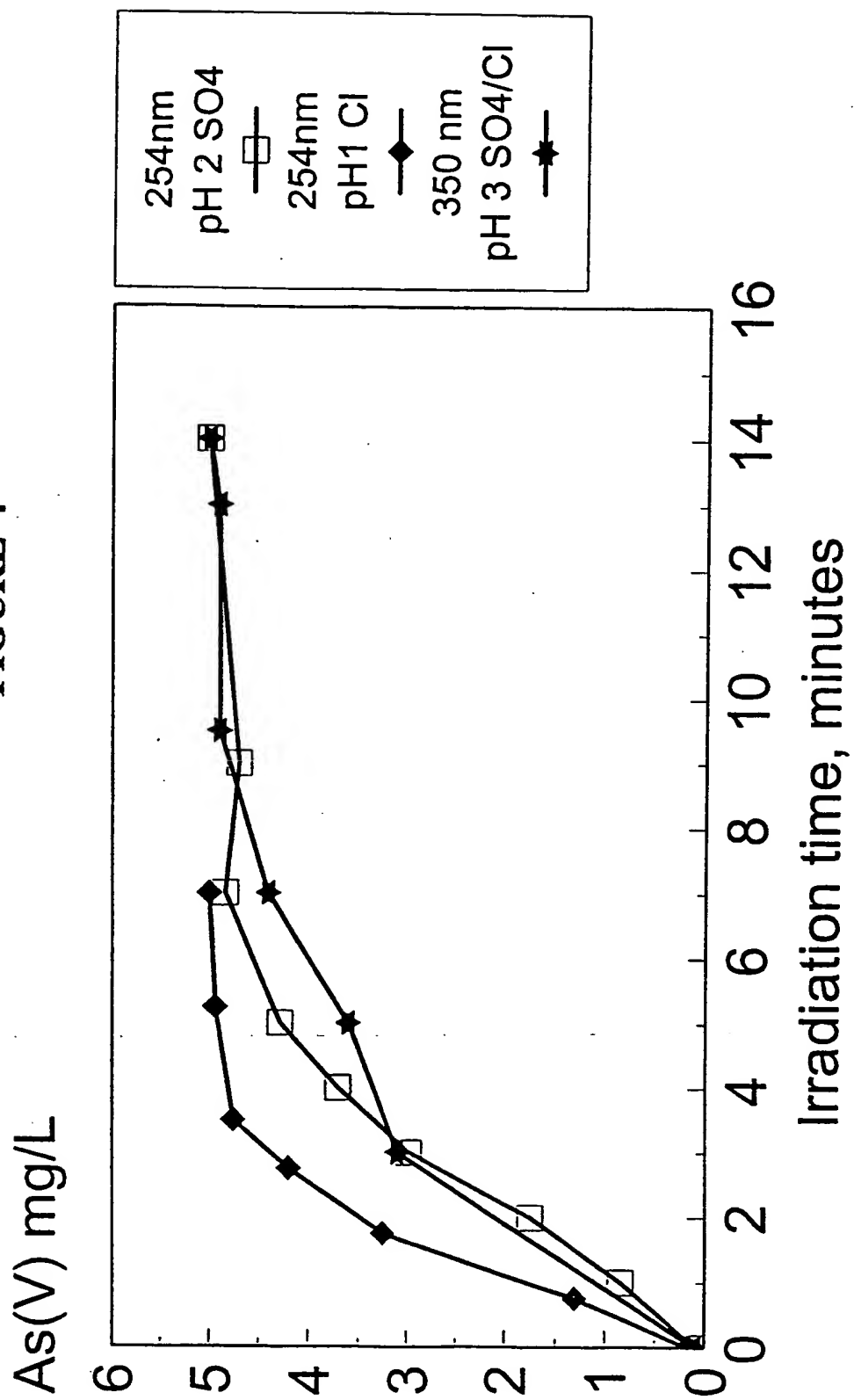
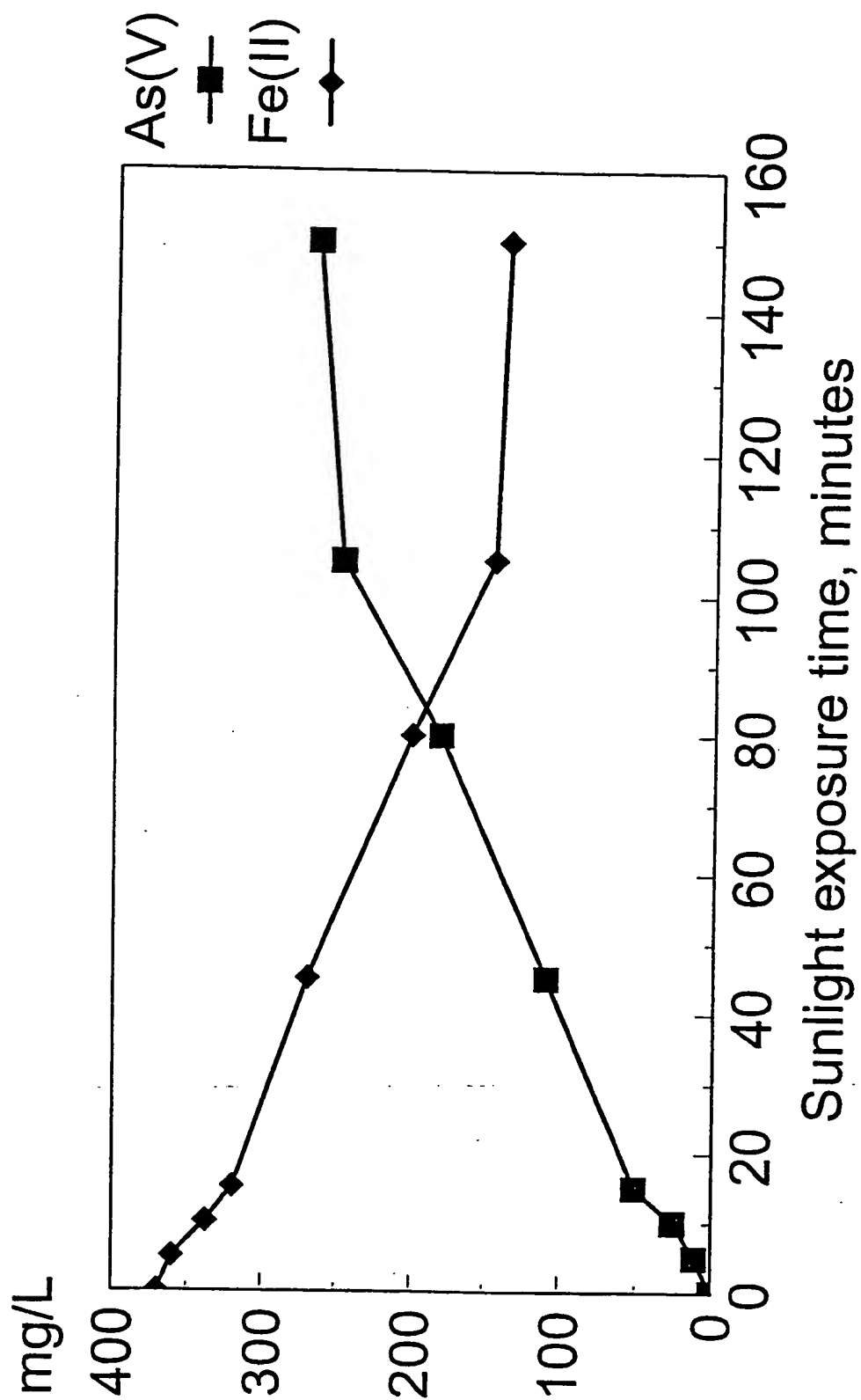


FIGURE 4



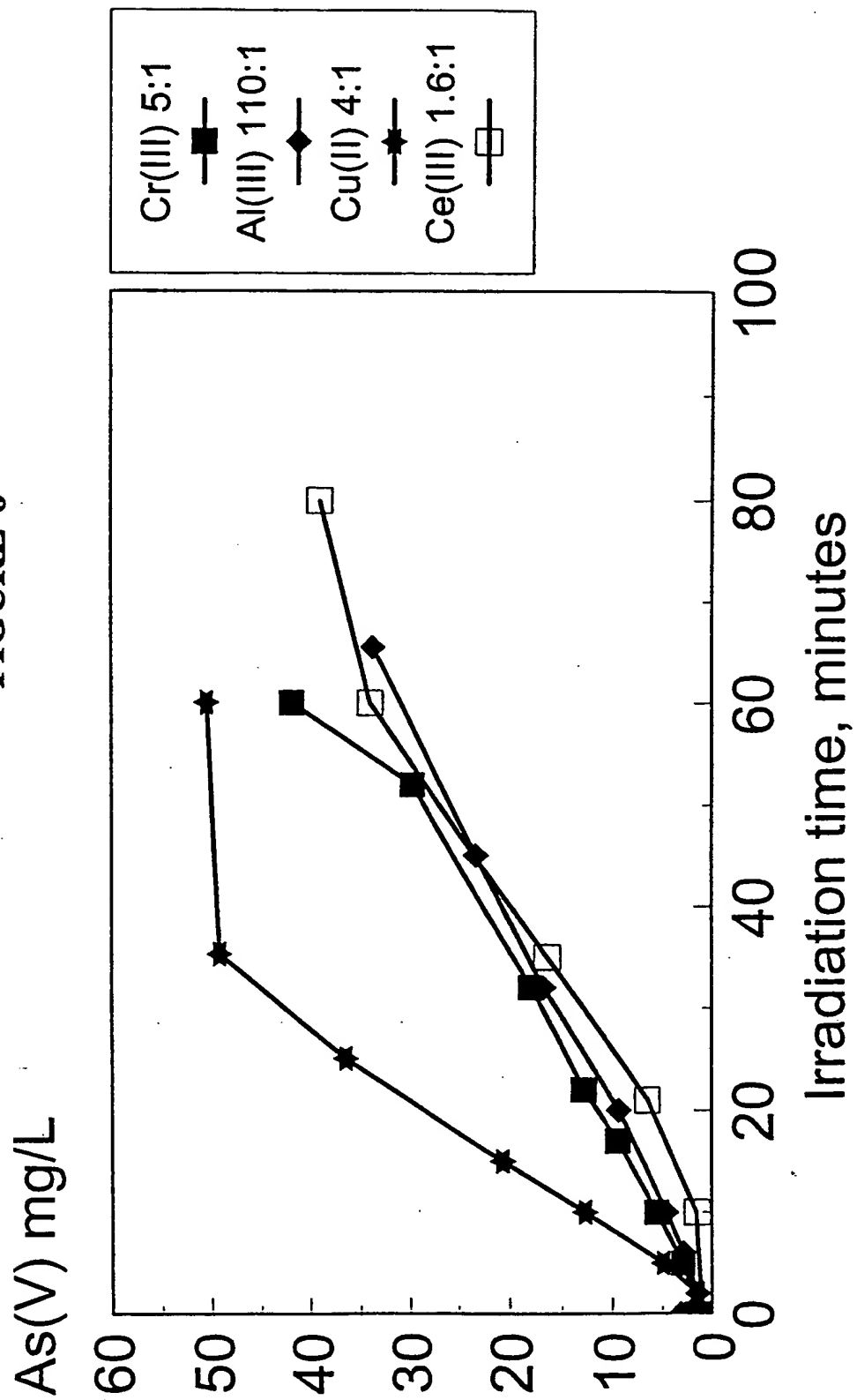
5 / 12

FIGURE 5



6 / 12

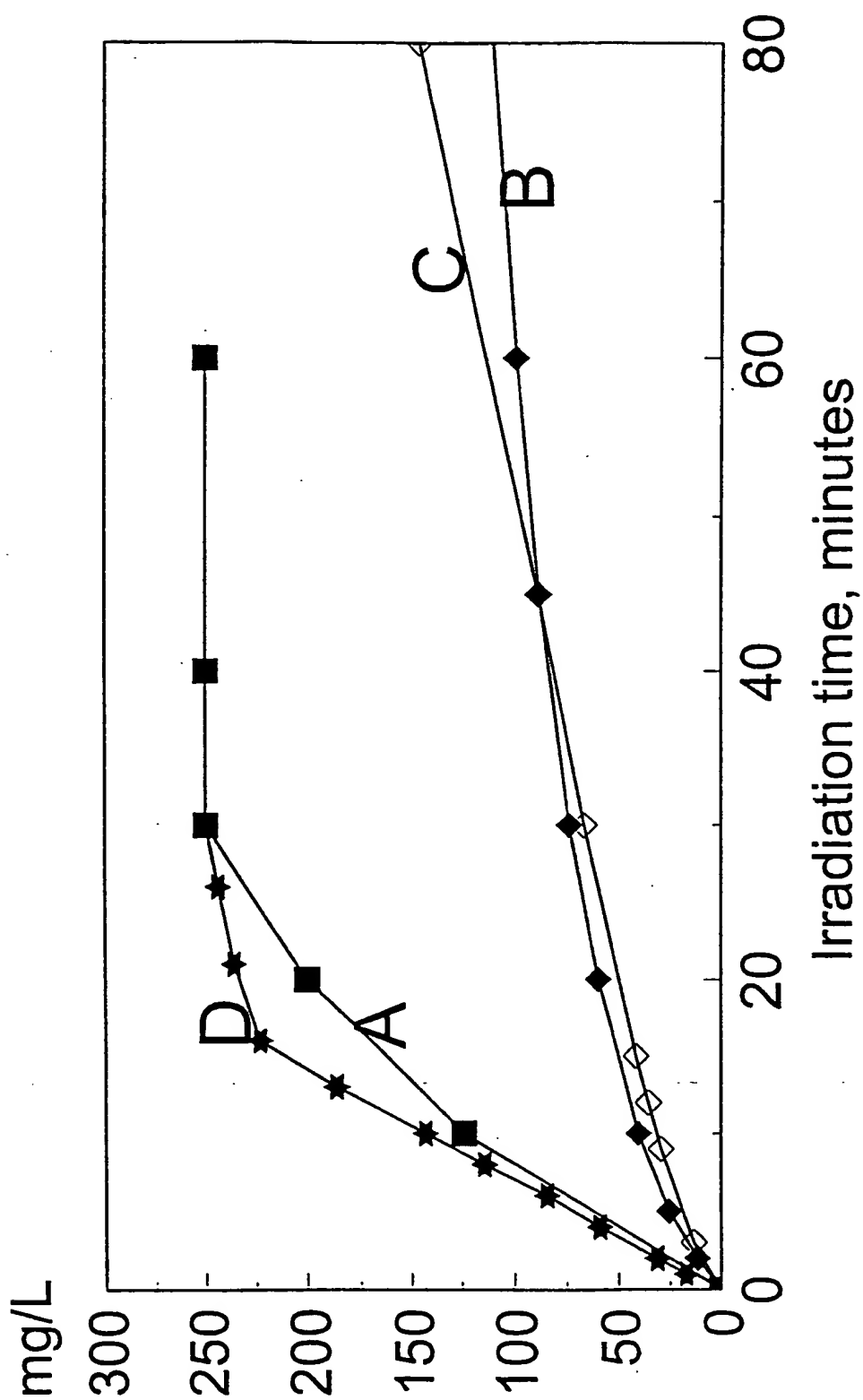
FIGURE 6





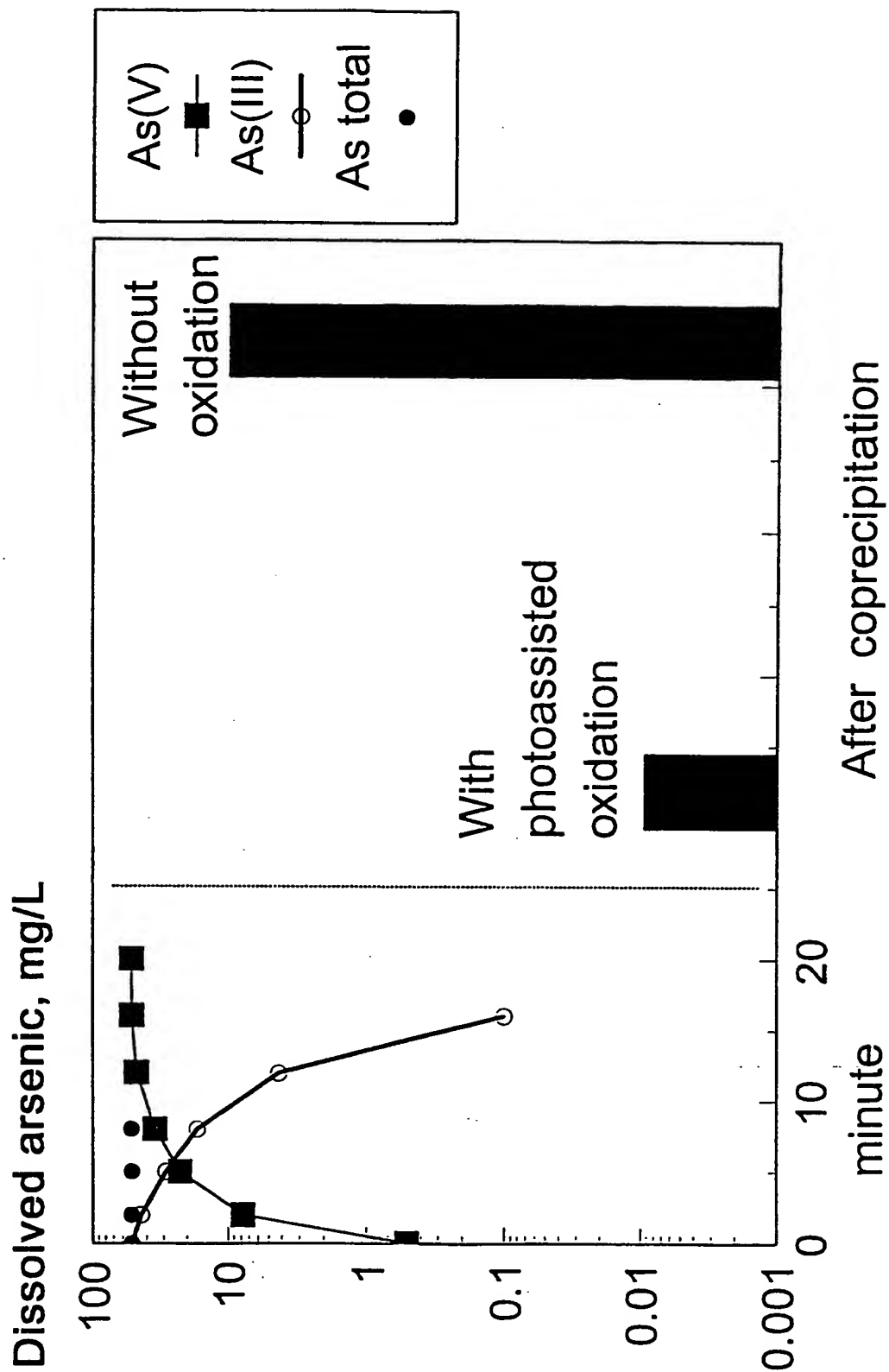
7 / 12

FIGURE 7



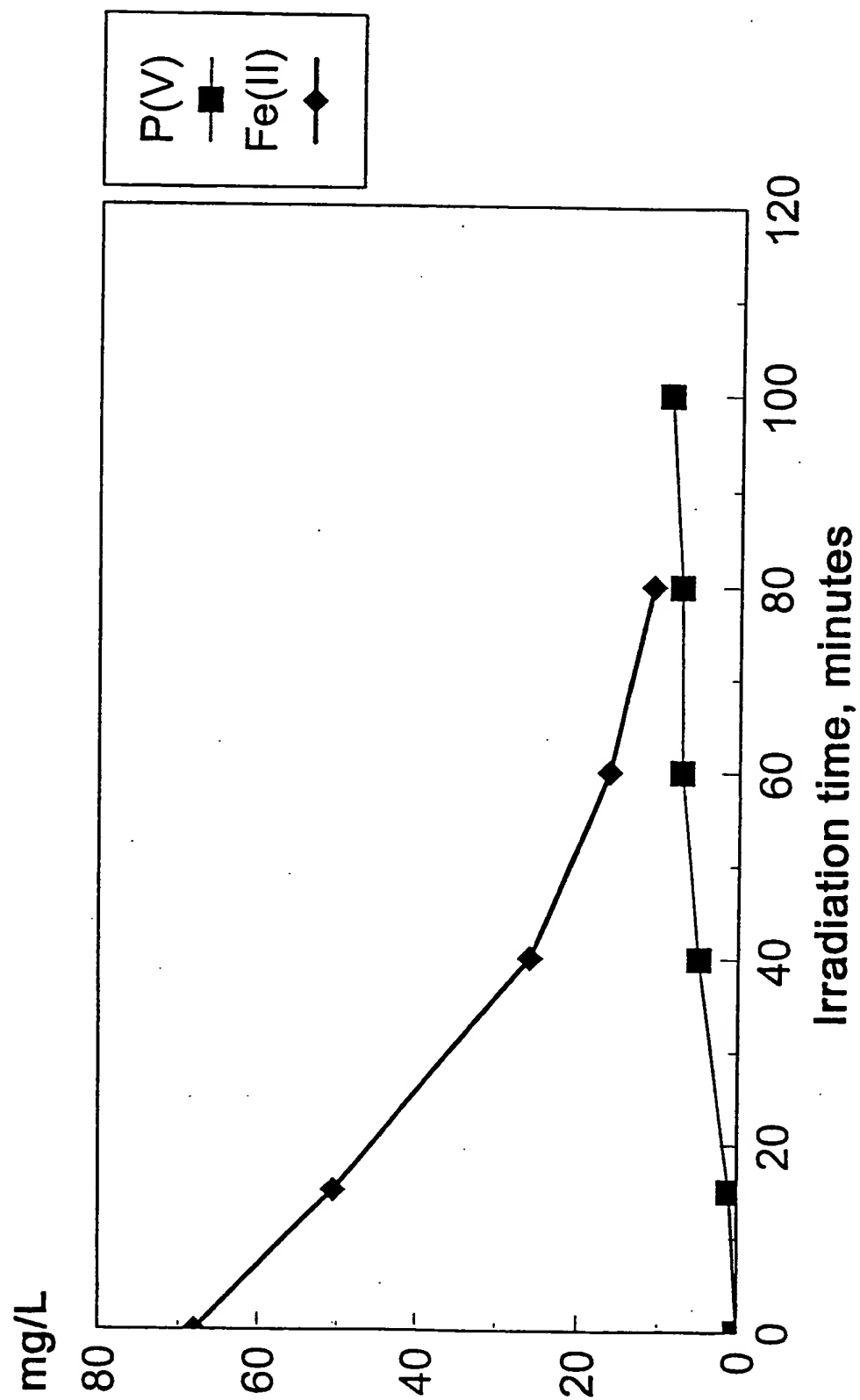
8 / 12

FIGURE 8



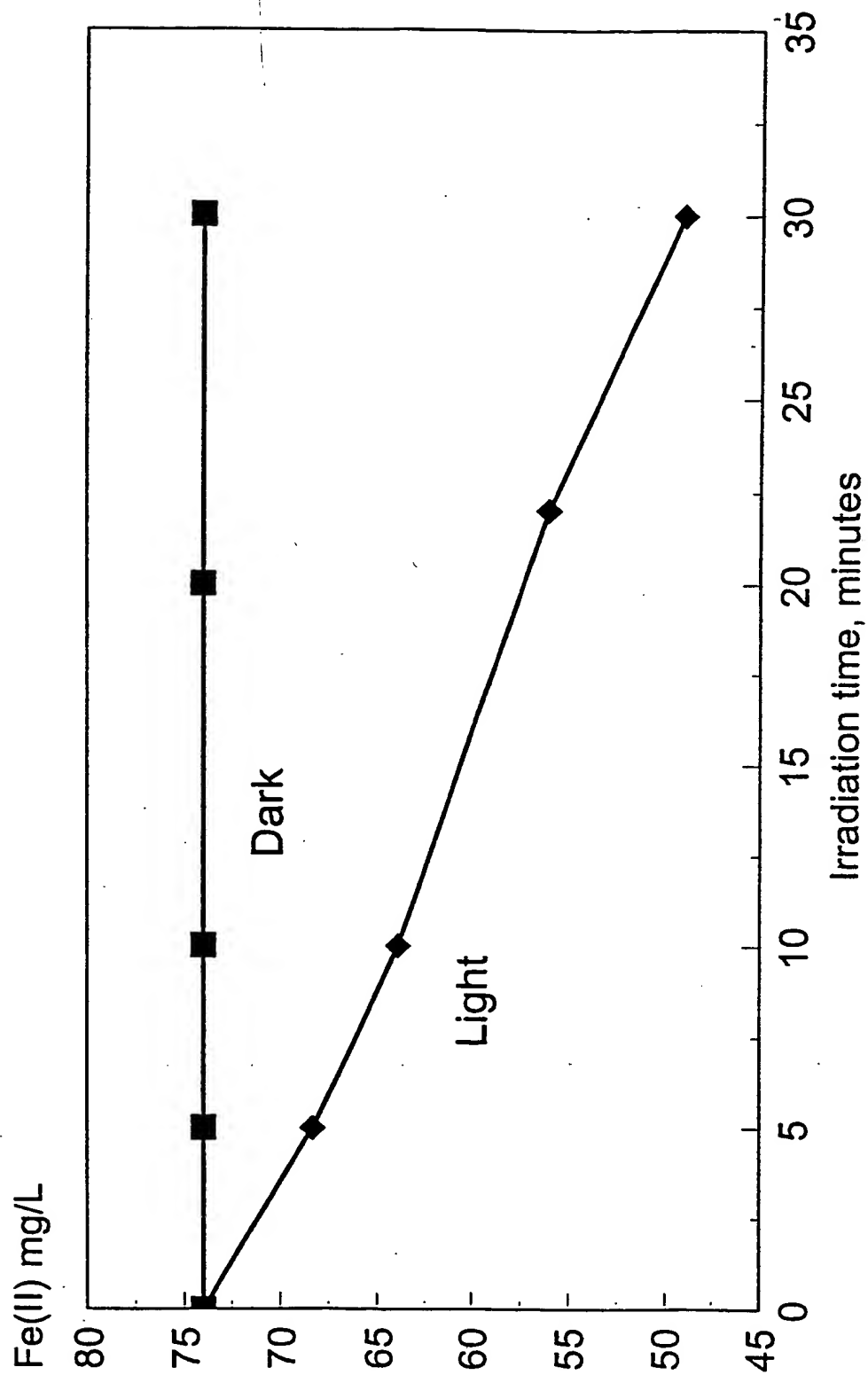
9 / 12

FIGURE 9



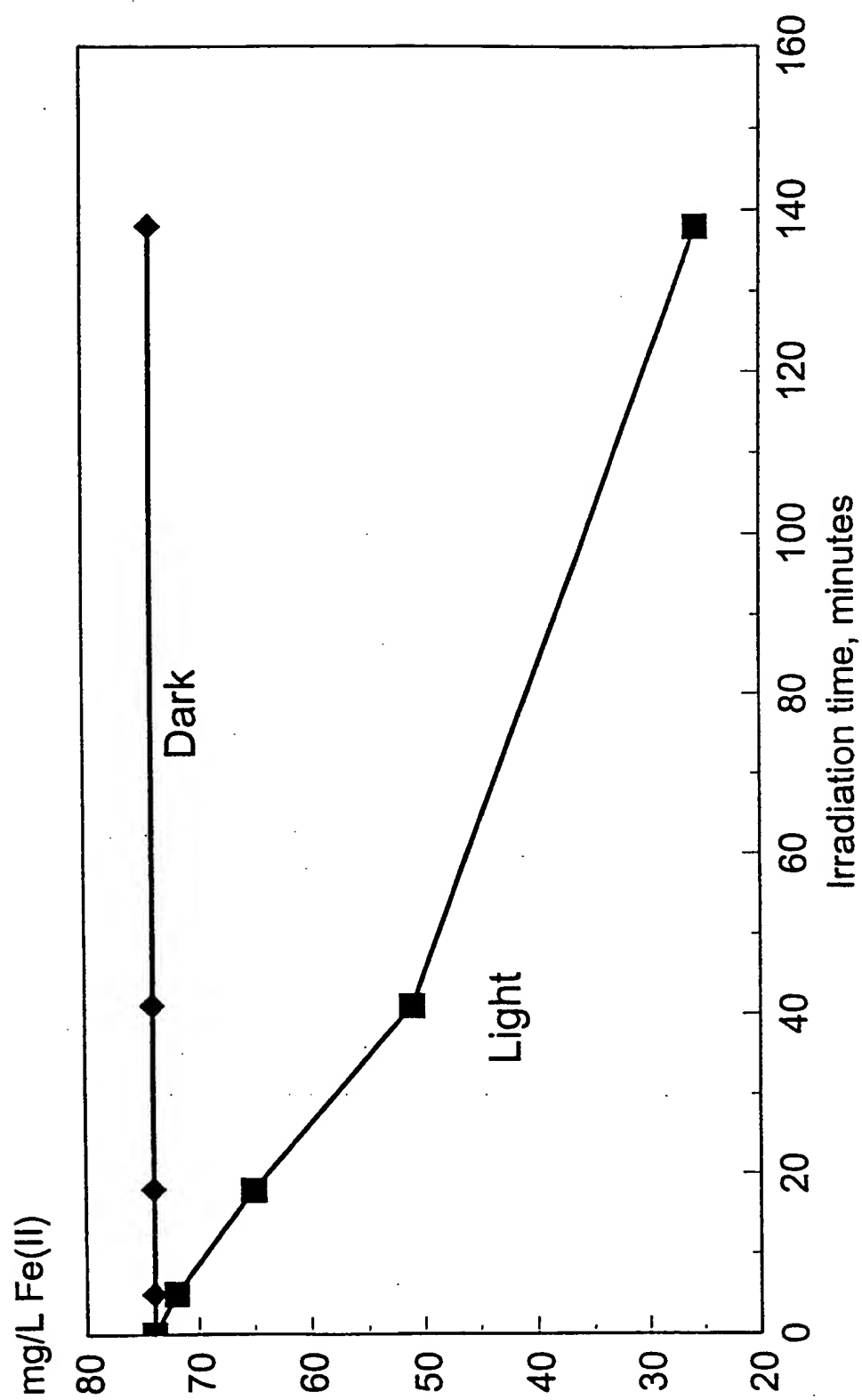
10 / 12

FIGURE 10



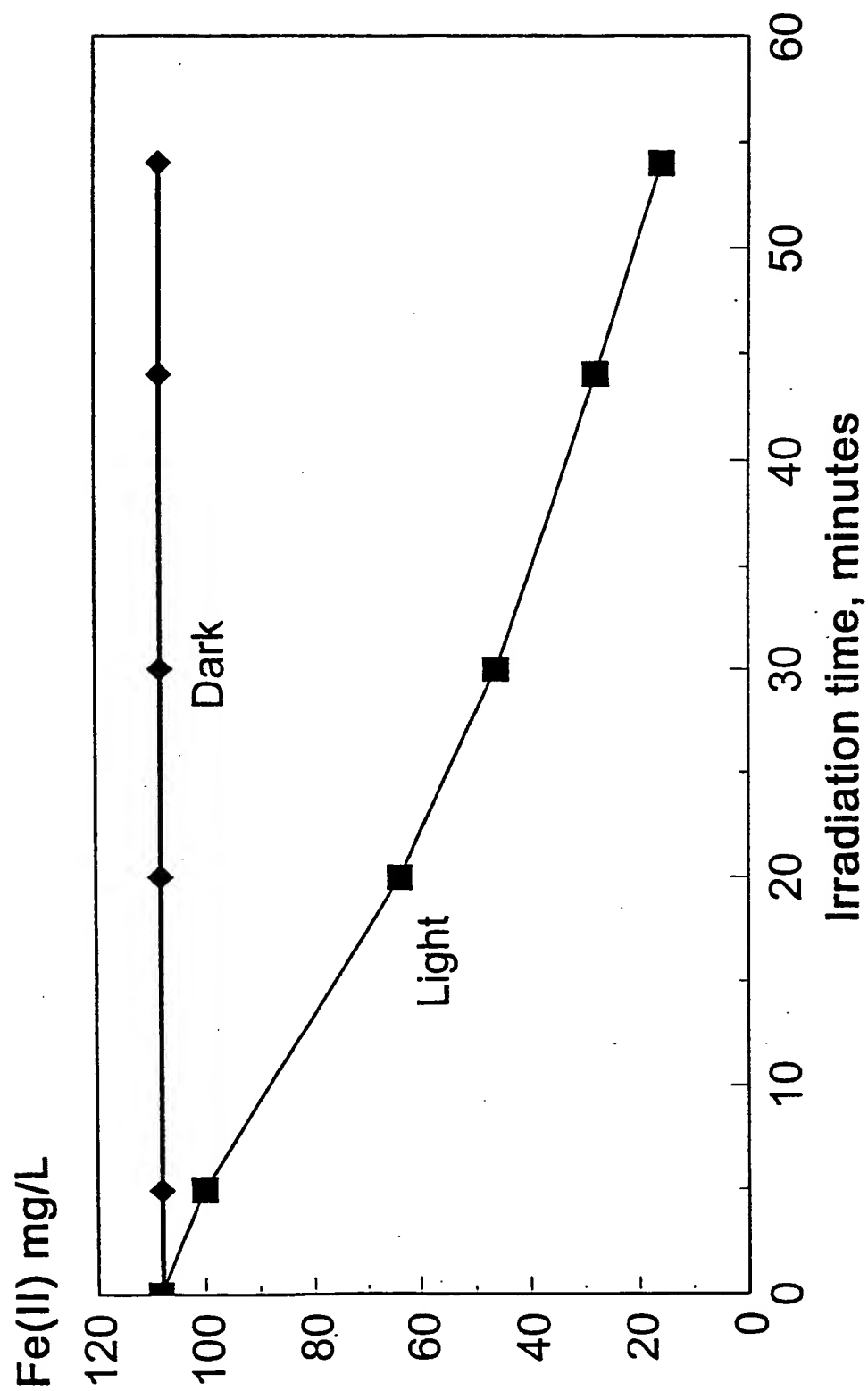
11 / 12

FIGURE 11



12 / 12

FIGURE 12



**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl.<sup>6</sup> C01B 25/12, C01G 28/00, C01G 49/06, C01B 17/74

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC C01B 25/12, C01G 28/00, C01G 49/06, C01B 17/74

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
AU: IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	NIL.	

☐Further documents are listed  
in the continuation of Box C.☐

See patent family annex.

**\* Special categories of cited documents :**

"A" document defining the general state of the art which is not considered to be of particular relevance  
"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

**"T"**later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
**"X"** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone**"Y"**

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

**"&"**

document member of the same patent family

Date of the actual completion of the international search

30 January 1995 (30.01.95)

Date of mailing of the international search report

7 Feb 1995 (7.2.95)

Name and mailing address of the ISA/AU

AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION  
PO BOX 200  
WODEN ACT 2606  
AUSTRALIA

Facsimile No. 06 2853929

Authorized officer

**G. CARTER**

Telephone No. (06) 2832154